

Mild, Efficient, and Metal-Free Radical 1,2-Dithiocyanation of Alkynes and Alkenes at Room Temperature

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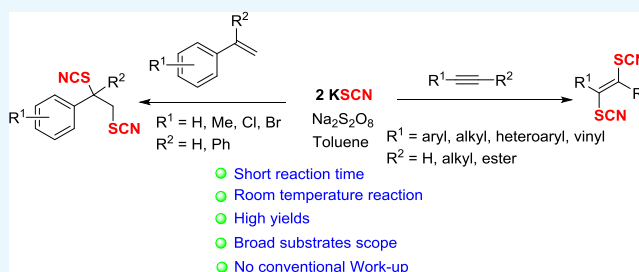
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Supporting Information

ABSTRACT: A transition metal-free process has been reported for 1,2-dithiocyanation of alkynes in the presence of sodium persulfate and potassium thiocyanate reagent combination in a short reaction time under ambient air. Styrene derivatives are equally applicable under the same reaction conditions. Monothiocyanated vinyl derivatives were also synthesized from 2-ethynylpyridine and dimethyl acetylene dicarboxylate. The reaction proceeds by the radical/polar pathway as evidenced from our experiments and literature. After removal of the solvent from the reaction mixture by evaporation, the crude product was purified without conventional workup.



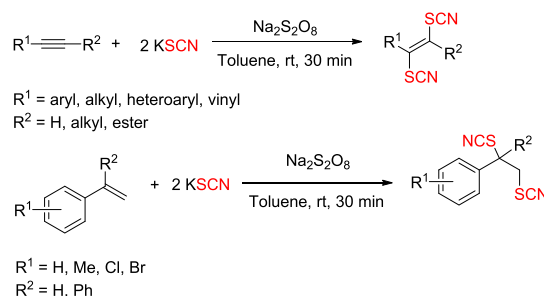
INTRODUCTION

Difunctionalization of organic substrates is a powerful tool in modern organic synthesis, which mainly involves alkynes as well as alkenes in organic synthesis.^{1–13} It has been widely studied and utilized in various techniques for functional group interconversions.^{14–17} Difunctionalization of alkenes is an attractive method for introducing a set of groups during a one-pot reaction process.^{18,19} Dithiocyanation of alkynes and alkenes is meaningful as they show fungicidal activity.²⁰ In addition, different sulfur derivatives can be synthesized from the thiocyanates.^{21–24} These can be easily converted to different compounds such as sulfides, disulfides, thioesters, thiols, thiocarbamates, and many sulfur heterocycles.^{25–34} Therefore, efficient incorporation of the thiocyno group into organic molecules has drawn much attention.

Few methods have been developed for the dithiocyanation of alkenes using different catalytic systems such as combination of $\text{PhI}(\text{OAc})_2$ /trialkylsilyl cyanide or potassium thiocyanate (KSCN) reagent,^{35,36} cerium(IV) ammonium nitrate-mediated thiocyanation of styrenes,³⁷ FeCl_3 ,³⁸ and recently Cu-catalyzed dithiocyanation in the presence of NH_4SCN and selectfluor reagent combination.³⁹ However, to the best of our knowledge, dithiocyanation of alkynes is very rare. Only one method has been reported previously.⁴⁰ It is worthy to mention that most of the previous methods suffer from at least one of the following general disadvantages such as low-to-moderate yields, lengthy reaction time, vigorous conditions, use of toxic as well as expensive metals, and complex reagent

combination. It should be mentioned that none of these methods are applicable for dithiocyanation of both alkynes and alkenes under fully similar conditions. Hence, the development of a new and common reagent system which is useful for synthesizing dithiocyanate derivatives from alkynes as well as alkenes is highly desirable. Therefore, in continuation of our research,^{41–47} herein we are pleased to report a simple and convenient process for the dithiocyanation of alkynes as well as alkenes in a short reaction time in the presence of potassium thiocyanate and sodium persulfate reagent combination (Scheme 1).

Scheme 1. Transition Metal-Free 1,2-Dithiocyanation of Alkynes and Alkenes



Received: July 24, 2018

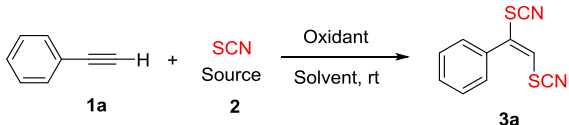
Accepted: September 28, 2018

Published: October 11, 2018

RESULTS AND DISCUSSION

This study was initiated by observing the reaction of 1 equiv of phenyl acetylene **1a** and 2 equiv of KSCN (**2**) employing 1 equiv of sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) as the oxidant in 1,2-dichloroethane (1,2-DCE) solvent at room temperature under ambient air for 30 min. Gratifyingly, the desired dithiocyanated coupling product, (1,2-dithiocyanatovinyl)benzene (**3a**), was obtained in a 55% yield after 30 min (Table 1, entry 1). This

Table 1. Optimization of the Reaction Conditions^a

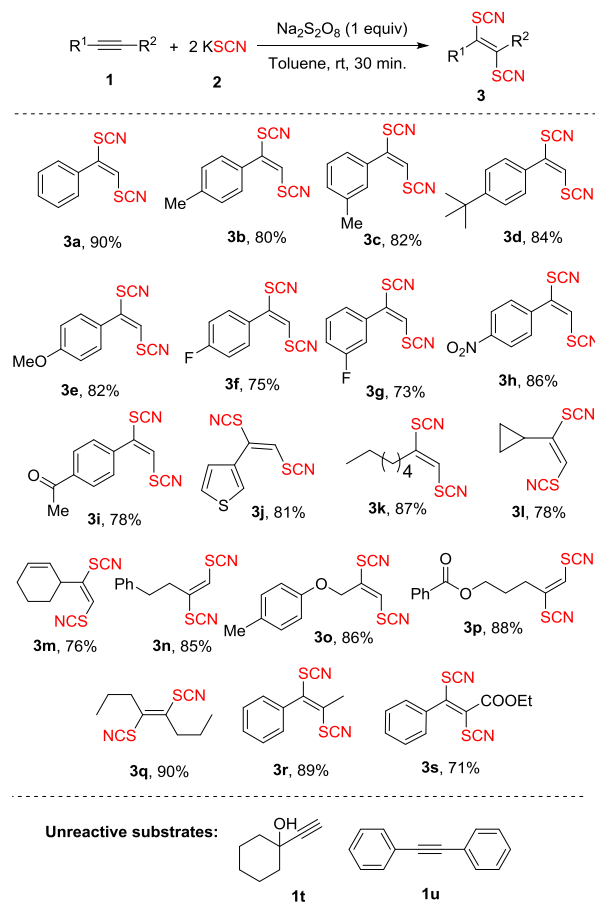
				
entry	source of SCN (equiv)	oxidant (equiv)	solvent (2 mL)	yields (%) ^b
1	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	1,2-DCE	55
2	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	DCM	85
3	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	THF	30
4	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	1,4-dioxane	<10
5	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	CH_3CN	20
6	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	DMF	<10
7	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	toluene	90, 92 ^c
8	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	DMSO	ND
9	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	PEG-400	ND
10	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	H_2O	ND
11	KSCN (2)	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ (1)	toluene	60
12	KSCN (2)	$\text{K}_2\text{S}_2\text{O}_8$ (1)	toluene	88
13	KSCN (2)	DTBP (1)	toluene	ND
14	NH_4SCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	toluene	70
15	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (2)	toluene	90
16	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (0.5)	toluene	48
17	KSCN (4)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	toluene	90
18	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	toluene	ND
19	KSCN (2)	$\text{Na}_2\text{S}_2\text{O}_8$ (1)	neat	ND

^aReaction conditions: carried out with 1 mmol of **1a** and 2 mmol of SCN source in 2 mL of solvent at room temperature for 30 min. ^bAll are isolated yields. ^cReaction time 12 h.

result encouraged us to optimize the reaction in different conditions, and the results are summarized in Table 1. To interpret the solvent effects, the reaction was examined in various solvents (Table 1, entries 2–10). To our pleasure, the desired product was isolated in an excellent yield (90%) in toluene after 30 min (Table 1, entry 7). The yield was not improved significantly by increasing the reaction time. Other common solvents such as dichloromethane (DCM), tetrahydrofuran (THF), 1,4-dioxane, CH_3CN , dimethylformamide (DMF), dimethyl sulfoxide (DMSO), poly(ethylene glycol) (PEG)-400, and water were not so effective. Other oxidants such as ammonium persulfate [$(\text{NH}_4)_2\text{S}_2\text{O}_8$], potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), and di-*tert*-butyl peroxide (DTBP) were also investigated. These were not so effective for this transformation (Table 1, entries 11–13). Ammonium thiocyanate (NH_4SCN), as the thiocyanate source, is also not effective for this transformation (Table 1, entry 14). A higher amount of oxidant loading (2 equiv) did not improve the yield further (Table 1, entry 15), but on decreasing the amount of oxidant (0.5 equiv), the yield was decreased considerably (Table 1, entry 16). In addition, by increasing the amount of KSCN, the yield was not improved (Table 1, entry

17). The reaction did not proceed at all in the absence of any oxidant (Table 1, entry 18) as well as under neat condition (Table 1, entry 19). Therefore, on the basis of the series of experiments (Table 1, entries 1–19), we considered the optimized reaction conditions by using 2 equiv of KSCN and 1 equiv of $\text{Na}_2\text{S}_2\text{O}_8$ in toluene for 30 min at room temperature under ambient air (Table 1, entry 7).

Considering the optimization of the reaction conditions, we examined the general applicability by increasing the substrate scope (Scheme 2). A series of 1,2-dithiocyanated alkenes were

Scheme 2. Substrate Scope for the 1,2-Dithiocyanation of Various Alkynes^a

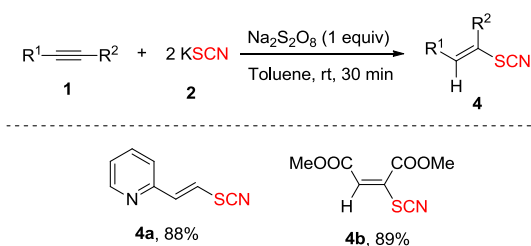
^aReaction conditions: **1** (1 mmol) and **2** (2 mmol) in the presence of 1 equiv of $\text{Na}_2\text{S}_2\text{O}_8$ in 2 mL of toluene for 30 min at room temperature.

obtained in good to excellent yields under the present reaction conditions (**3a–3s**). Phenyl alkynes with electron-donating substituents on the benzene ring (such as $-\text{Me}$, $-\text{tert-butyl}$, and $-\text{OMe}$) afforded the corresponding 1,2-dithiocyanated alkenes in excellent yields (**3b**, **3c**, **3d**, and **3e**). Electron-withdrawing substituents on the benzene ring of the phenyl acetylene moiety (such as $-\text{F}$ and $-\text{NO}_2$) efficiently reacted with KSCN to produce the respective 1,2-dithiocyanated alkene derivatives (**3f**, **3g**, and **3h**). Carbonyl functionality is also well tolerated to afford the desired product in good yield (**3i**). Heteroaryl-substituted terminal alkyne (such as 3-ethynylthiophene **1j**) also reacted smoothly under the optimized reaction conditions (**3j**). In addition, aliphatic terminal alkynes were also found to afford the desired products in high yields (**3k–3n**). Apart from

aryl acetylenes, alkenyl acetylene (**1m**) is also a good substrate for the reaction. Two oxy-substituted terminal alkynes were also tested; they also furnished the desired products in excellent yields (**3o** and **3p**).

It is worthy to mention that the present reaction conditions are equally effective for internal alkynes. We have examined three different internal alkynes such as oct-4-yne (**1q**), prop-1-yn-1-ylbenzene (**1r**), and ethyl 3-phenylpropiolate (**1s**); all of these afforded the desired products (**3q–3s**) in excellent yields. However, 1-ethynylcyclohexan-1-ol (**1t**) and 1,2-diphenylethyne (**1u**) remained unreacted under the present reaction conditions. During our studies on the substrate scope, we have selectively found the 1,2-dithiocyanation product. Only the formation of monothiocyanated alkene derivatives (**4a** and **4b**) has been observed in cases of 2-ethynylpyridine and dimethyl acetylene dicarboxylate in 88 and 89% yields, respectively (Scheme 3).

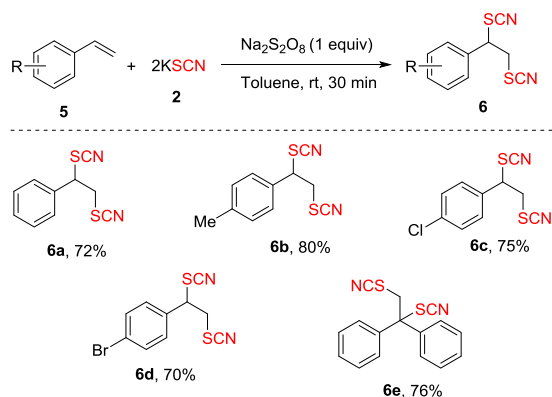
Scheme 3. Formation of Monothiocyanated Vinyl Derivatives^a



^aReaction conditions: **1** (1 mmol) and **2** (2 mmol) in the presence of 1 equiv of $\text{Na}_2\text{S}_2\text{O}_8$ in 2 mL of toluene for 30 min at room temperature.

To explore the scope of the present methodology, we used styrene derivatives to synthesize diverse vicinal dithiocyanate derivatives (Scheme 4). Styrenes **5** with different substituents on the aromatic ring, including electron-donating and electron-withdrawing groups, can be transformed into the corresponding products **6** in good yields. Styrene having a $-\text{Me}$ substituent on the benzene ring reacted with KSCN efficiently to afford the product with good yield (**6b**). Halo-substituted

Scheme 4. Synthesis of Diverse Vicinal Dithiocyanate Derivatives from Styrenes^a

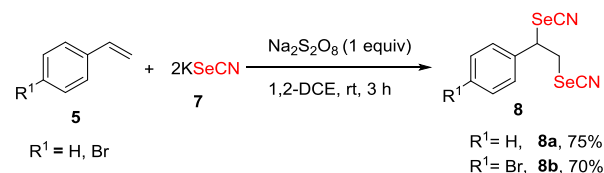


^aReaction conditions: 1 mmol of **5** and 2 mmol of **2** in the presence of 1 equiv of $\text{Na}_2\text{S}_2\text{O}_8$ in 2 mL of toluene at room temperature for 30 min.

styrenes were well tolerated in the dithiocyanation reaction (**6c** and **6d**). In addition, we are pleased to notice that 1,1-diphenylethyne (DPE) gave the desired product (**6e**) with good yields under the stated reaction conditions. To make the reaction more greener aspect, we tried the reaction for both alkyne and alkene by light in the presence of a photocatalyst instead of persulfate. The desirable product for alkyne was found with low yield, whereas for styrene no satisfactory product has been isolated (see the Supporting Information).

As an application, we observed that this protocol is extendable for diselenylation of styrenes using KSeCN instead of KSCN with a combination of similar reagents (Scheme 5).

Scheme 5. Diselenylation of Styrenes Using Potassium Selenocyanate^a



^aReaction conditions: **5** (1 mmol) and **7** (2 mmol) in the presence of 1 equiv of $\text{Na}_2\text{S}_2\text{O}_8$ in 2 mL of 1,2-DCE for 3 h at room temperature.

All these reactions are not sensitive to air and moisture and were performed under an open atmosphere. The reaction conditions are mild enough and found no decomposition or polymerization of the starting materials. We have not observed any considerable byproducts for all reactions studied. All of the synthesized compounds have been characterized by spectral data and the new compounds by spectral and analytical data. X-ray crystallographic analysis of ethyl (*E*)-3-phenyl-2,3-dithiocyanatoacrylate (**3s**) was performed to confirm the structure of the product as shown in Figure 1.⁴⁸ In addition, we

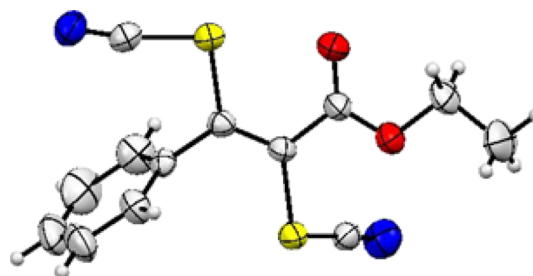
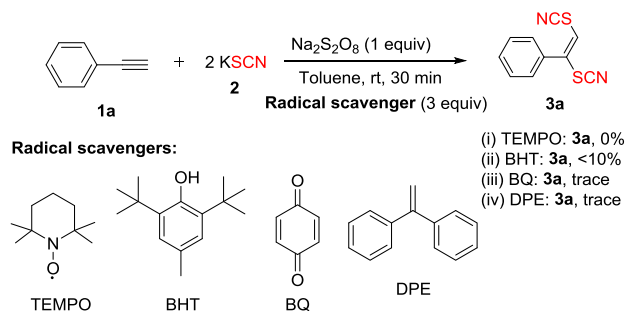


Figure 1. X-ray crystal structure of compound **3s**.

have also carried out correlation spectroscopy and nuclear Overhauser effect NMR experiment of compound **3c** where we did not find any cross-peak and trans-conformation was confirmed. For this present reaction, the workup procedure can be avoided. The solvent (toluene) was evaporated under rotary evaporator after completion of the reaction, and the crude reaction mixture was purified by column chromatography using silica gel.

To get a better understanding of the mechanism of this reaction, few control experiments were carried out (Scheme 6). In the presence of radical scavengers such as (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and butylated hydroxytoluene (BHT), no product was obtained, whereas a trace amount of product was obtained in the presence of 1,4-

Scheme 6. Control Experiments^a

^aReaction conditions: **1a** (1 mmol), KSCN (2 mmol), and 3 mmol of different radical scavengers in the presence of 1 equiv of Na₂S₂O₈ in 2 mL of toluene for 30 min at room temperature.

benzoquinone (BQ) and DPE. These results suggest that the reaction probably proceeds through a radical pathway.

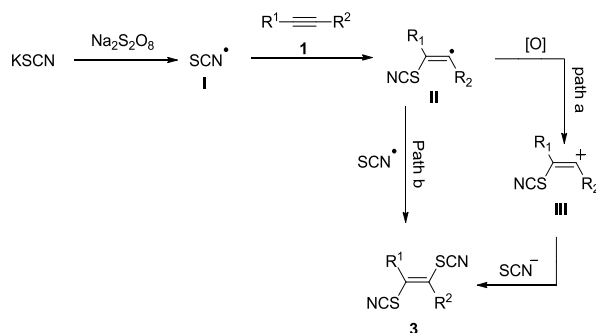
In a mixture (1:1) of phenyl acetylene (**1a**) and DPE (**5e**) with 2 equiv of KSCN when subjected to react under the same reaction conditions, only the DPE (**5e**) participated in the reaction to afford the desired product (**6e**), whereas compound **3a** was isolated as trace amount (Scheme 7). Therefore, the reaction is selective and shows the high reactivity of alkenes than alkynes. In other words, we can say that here DPE (**5e**) acts as a radical scavenger, which also proves that the reaction goes through a radical pathway.

On the basis of the above experimental results and literature,^{35–37,49–53} a plausible mechanism is proposed in Scheme 8. Initially, an electrophilic thiocyanate radical I is generated by the oxidation of thiocyanate anion by Na₂S₂O₈. Subsequent radical addition of I to alkyne derivative (**1**) produces carbon-centered radical II, which was further oxidized to the corresponding carbocation III by Na₂S₂O₈. Then, the nucleophilic reaction of thiocyanate anion (path a) with the carbocation III forms the desired product **3**. Another pathway is possible (path b), which involves the coupling of thiocyanate radical with intermediate II to form the desired product **3**.

CONCLUSIONS

In summary, we have developed a mild and metal-free method for the 1,2-dithiocyanation of alkynes in a short reaction time using the reagent combination of sodium persulfate and potassium thiocyanate. A variety of 1,2-dithiocyanated alkene derivatives have been synthesized with broad functionalities in high yields. The present methodology is also useful for the dithiocyanation of styrene derivatives to provide a variety of vicinal dithiocyanate derivatives. We also observed the formation of monothiocyanated vinyl derivatives in cases of 2-ethynylpyridine and dimethyl acetylenedicarboxylate. The selectivity of this reaction was also tested by carrying out the reaction between phenyl acetylene and DPE. We believe that our present methodology is a meaningful addition over the

Scheme 8. Proposed Reaction Mechanism



existing methods to synthesize important building blocks of 1,2-dithiocyanated alkene and alkane derivatives.

EXPERIMENTAL SECTION

General. All substrates and reagents we have used in the experiment were purchased from commercial sources and used without any purification. ¹H NMR spectra were recorded using a 400 MHz spectrometer, and CDCl₃ was used as the solvent. Chemical shifts were expressed in parts per million (ppm) (δ) and coupling constants (*J*) were given in hertz, whereas the signals were represented as s (singlet), d (doublet), t (triplet), m (multiplet), and dd (double doublet). ¹³C NMR spectra were recorded at 100 MHz, and ⁷⁷Se NMR spectra were recorded at 76 MHz in CDCl₃ solution. Chemical shifts as internal standard were referenced to CDCl₃ (δ = 7.26 for ¹H and δ = 77.16 for ¹³C NMR). Precoated silica gel on an aluminum foil was used for thin layer chromatography (TLC) with dried and distilled solvent before use.

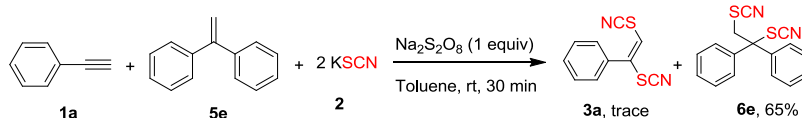
General Procedure for the Synthesis of Compounds

3. A mixture of alkyne (**1**, 1 mmol), KSCN (194 mg, 2 mmol), and sodium persulfate (238 mg, 1 mmol) was taken in a dry sealed tube, and 2 mL of toluene was added to this mixture. The resulting mixture was stirred at room temperature for 30 min. After completion of the reaction (TLC), the crude product was isolated just by evaporation of the solvent (toluene) in a rotary evaporator under reduced pressure. No conventional workup procedure has been followed. The crude reaction mixture was purified by column chromatography on silica gel (60–120 mesh) using petroleum ether and ethyl acetate as eluents.

General Procedure for the Synthesis of Compounds

6. A mixture of alkene (**5**, 1 mmol), KSCN (194 mg, 2 mmol), and sodium persulfate (238 mg, 1 mmol) was taken in a dry sealed tube. Toluene (2 mL) was added to the mixture, and the resulting mixture was stirred at room temperature for 30 min. After completion of the reaction (TLC), the solvent (toluene) was evaporated in a rotary evaporator under reduced pressure, and the crude reaction mixture was purified by column chromatography on silica gel (60–120 mesh) using petroleum ether and ethyl acetate as eluents.

Scheme 7. Competitive Reaction between Alkynes and Alkenes



(*E*)-(1,2-Dithiocyanatovinyl)benzene (**3a**).⁴⁰ Colorless solid (196 mg, 90%), mp 63–65 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.52–7.49 (m, 3H), 7.39–7.36 (m, 2H), 6.81 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 131.8, 131.4, 129.7, 128.6, 127.5, 117.2, 108.7, 107.9.

(*E*)-1-(1,2-Dithiocyanatovinyl)-4-methylbenzene (**3b**).⁴⁰ Colorless solid (185 mg, 80%), mp 92–94 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.32–7.25 (m, 4H), 6.76 (s, 1H), 2.41 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 142.1, 131.8, 130.4, 128.9, 128.6, 116.3, 109.0, 108.2, 21.7.

(*E*)-1-(1,2-Dithiocyanatovinyl)-3-methylbenzene (**3c**). Light yellow oil (190 mg, 82%); ¹H NMR (CDCl₃, 400 MHz): δ 7.40–7.36 (m, 1H), 7.34–7.30 (m, 1H), 7.17–7.15 (m, 2H), 6.78 (s, 1H), 2.41 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 139.9, 132.3, 131.7, 129.6, 129.0, 125.8, 116.7, 108.9, 108.1, 21.5. Anal. Calcd for C₁₁H₈N₂S₂: C, 56.87; H, 3.47; N, 12.06%. Found: C, 56.77; H, 3.41; N, 12.02%.

(*E*)-1-(*tert*-Butyl)-4-(1,2-dithiocyanatovinyl)benzene (**3d**). Pale yellow gummy mass (230 mg, 84%); ¹H NMR (CDCl₃, 400 MHz): δ 7.51–7.47 (m, 2H), 7.31–7.29 (m, 2H), 6.77 (s, 1H), 1.34 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz): δ 155.1, 131.6, 128.8, 128.5, 126.7, 116.3, 109.0, 108.2, 35.2, 31.2. Anal. Calcd for C₁₄H₁₄N₂S₂: C, 61.28; H, 5.14; N, 10.21%. Found: C, 61.20; H, 5.21; N, 10.32%.

(*E*)-1-(1,2-Dithiocyanatovinyl)-4-methoxybenzene (**3e**). Pale yellow gummy mass (203 mg, 82%); ¹H NMR (CDCl₃, 400 MHz): δ 7.33–7.31 (m, 2H), 7.00–6.98 (m, 2H), 6.71 (s, 1H), 3.86 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 161.9, 131.8, 130.4, 123.7, 115.6, 115.1, 109.0, 108.2, 55.6. Anal. Calcd for C₁₁H₈N₂OS₂: C, 53.21; H, 3.25; N, 11.28%. Found: C, 53.14; H, 3.13; N, 11.20%.

(*E*)-1-(1,2-Dithiocyanatovinyl)-4-fluorobenzene (**3f**). Pale yellow oil (177 mg, 75%); ¹H NMR (CDCl₃, 400 MHz): δ 7.41–7.38 (m, 2H), 7.24–7.17 (m, 2H), 6.82 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 164.2 (d, ¹J_{C–F} = 253 Hz), 131.0 (d, ⁴J_{C–F} = 9 Hz), 130.7, 129.8, 127.9, 117.9, 117.2 (d, ²J_{C–F} = 22 Hz), 108.4, 107.7. Anal. Calcd for C₁₀H₅FN₂S₂: C, 50.83; H, 2.13; N, 11.86%. Found: C, 50.88; H, 2.06; N, 11.81%.

(*E*)-1-(1,2-Dithiocyanatovinyl)-3-fluorobenzene (**3g**). Yellow oil (172 mg, 73%); ¹H NMR (CDCl₃, 400 MHz): δ 7.53–7.47 (m, 1H), 7.25–7.16 (m, 2H), 7.14–7.10 (m, 1H), 6.88 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 163.0 (d, ¹J_{C–F} = 249 Hz), 133.8, 133.7, 131.7 (d, ⁴J_{C–F} = 8 Hz), 131.2, 129.8, 126.1, 124.6 (d, ³J_{C–F} = 3 Hz), 119.1, 118.8, 118.6, 115.9 (d, ²J_{C–F} = 23 Hz), 108.3, 107.6. Anal. Calcd for C₁₀H₅FN₂S₂: C, 50.83; H, 2.13; N, 11.86%. Found: C, 50.89; H, 2.04; N, 11.80%.

(*E*)-1-(1,2-Dithiocyanatovinyl)-4-nitrobenzene (**3h**). Yellow gummy mass (226 mg, 86%); ¹H NMR (CDCl₃, 400 MHz): δ 8.40–8.36 (m, 2H), 7.64–7.60 (m, 2H), 7.02 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 138.0, 130.1, 128.4, 125.0, 124.7, 121.5, 107.4, 107.1. Anal. Calcd for C₁₀H₅N₃O₂S₂: C, 45.62; H, 1.91; N, 15.96%. Found: C, 45.54; H, 1.82; N, 15.88%.

(*E*)-1-(4-(1,2-Dithiocyanatovinyl)phenyl)ethanone (**3i**). Pale yellow gummy mass (203 mg, 78%); ¹H NMR (CDCl₃, 400 MHz): δ 8.09–8.06 (m, 2H), 7.52–7.49 (m, 2H), 6.92 (s, 1H), 2.64 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 196.8, 139.1, 136.1, 130.4, 129.6, 129.1, 119.5, 108.1, 107.5, 26.8. Anal. Calcd for C₁₂H₈N₂OS₂: C, 55.37; H, 3.10; N, 10.76%. Found: C, 55.30; H, 3.02; N, 10.71%.

(*E*)-3-(1,2-Dithiocyanatovinyl)thiophene (**3j**). Yellow oil (181 mg, 81%); ¹H NMR (CDCl₃, 400 MHz): δ 7.57–7.56

(m, 1H), 7.51–7.49 (m, 1H), 7.22–7.21 (m, 1H), 6.78 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 132.3, 128.7, 128.4, 126.7, 125.9, 117.3, 108.6, 108.1. Anal. Calcd for C₈H₄N₂S₂: C, 42.84; H, 1.80; N, 12.49%. Found: C, 42.74; H, 1.72; N, 12.41%.

(*E*)-1,2-Dithiocyanatoct-1-ene (**3k**). Pale yellow oil (196 mg, 87%); ¹H NMR (CDCl₃, 400 MHz): δ 6.48 (s, 1H), 2.52 (t, *J* = 7.6 Hz, 2H), 1.61–1.58 (m, 2H), 1.32–1.31 (m, 6H), 0.91–0.88 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 136.7, 114.3, 108.4, 107.8, 33.1, 31.4, 28.5, 27.4, 22.5, 14.1. Anal. Calcd for C₁₀H₁₄N₂S₂: C, 53.06; H, 6.23; N, 12.38%. Found: C, 53.01; H, 6.16; N, 12.30%.

(*E*)-(1,2-Dithiocyanatovinyl)cyclopropane (**3l**). Light yellow oil (142 mg, 78%); ¹H NMR (CDCl₃, 400 MHz): δ 6.58 (d, *J* = 1.6 Hz, 1H), 1.77–1.71 (m, 1H), 1.11–1.06 (m, 2H), 0.90–0.86 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 133.8, 117.6, 108.7, 108.4, 14.0, 8.1. Anal. Calcd for C₇H₆N₂S₂: C, 46.13; H, 3.32; N, 15.37%. Found: C, 46.07; H, 3.24; N, 15.27%.

(*E*)-3-(1,2-Dithiocyanatovinyl)cyclohex-1-ene (**3m**).⁴⁰ Pale yellow liquid (168 mg, 76%); ¹H NMR (CDCl₃, 400 MHz): δ 6.48 (m, 1H), 5.95–5.93 (m, 1H), 2.23–2.17 (m, 4H), 1.78–1.72 (m, 2H), 1.69–1.64 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 136.5, 133.8, 131.9, 116.9, 109.4, 108.3, 26.5, 25.6, 22.1, 21.3.

(*E*)-(3,4-Dithiocyanatobut-3-en-1-yl)benzene (**3n**). Pale yellow oil (209 mg, 85%); ¹H NMR (CDCl₃, 400 MHz): δ 7.27–7.17 (m, 3H), 7.10–7.07 (m, 2H), 6.38 (s, 1H), 2.86–2.83 (m, 2H), 2.78–2.74 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 138.2, 134.7, 129.1, 128.9, 128.7, 127.3, 116.7, 108.4, 107.7, 35.2, 33.3. Anal. Calcd for C₁₂H₁₀N₂S₂: C, 58.51; H, 4.09; N, 11.37%. Found: C, 58.43; H, 4.02; N, 11.31%.

(*E*)-1-((2,3-Dithiocyanatoallyl)oxy)-4-methylbenzene (**3o**). Yellow solid (225 mg, 86%), mp 50–52 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.16–7.14 (m, 2H), 6.85–6.82 (m, 2H), 6.80 (s, 1H), 4.86 (d, *J* = 1.2 Hz, 2H), 2.32 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 154.5, 132.5, 130.4, 127.2, 120.9, 114.6, 109.2, 107.8, 67.5, 20.5. Anal. Calcd for C₁₂H₁₀N₂OS₂: C, 54.94; H, 3.84; N, 10.68%. Found: C, 54.83; H, 3.80; N, 10.61%.

(*E*)-4,5-Dithiocyanatopent-4-en-1-yl benzoate (**3p**). Pale yellow oil (267 mg, 88%); ¹H NMR (CDCl₃, 400 MHz): δ 8.05–8.02 (m, 2H), 7.60–7.56 (m, 1H), 7.47–7.43 (m, 2H), 6.55 (s, 1H), 4.35 (t, *J* = 6.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.12–2.09 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 166.3, 134.8, 133.3, 129.7, 129.6, 128.6, 116.4, 107.9, 107.4, 62.9, 29.8, 26.4. Anal. Calcd for C₁₄H₁₂N₂O₂S₂: C, 55.24; H, 3.97; N, 9.20%. Found: C, 55.20; H, 3.91; N, 9.12%.

(*E*)-4,5-Dithiocyanatoct-4-ene (**3q**). Colorless solid (203 mg, 90%), mp 53–55 °C; ¹H NMR (CDCl₃, 400 MHz): δ 2.71 (t, *J* = 7.6 Hz, 4H), 1.71–1.65 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 130.8, 108.4, 37.7, 21.4, 13.4. Anal. Calcd for C₁₀H₁₄N₂S₂: C, 53.06; H, 6.23; N, 12.38%. Found: C, 53.01; H, 6.29; N, 12.47%.

(*E*)-(1,2-Dithiocyanatoprop-1-en-1-yl)benzene (**3r**). Yellow oil (206 mg, 89%); ¹H NMR (CDCl₃, 400 MHz): δ 7.50–7.45 (m, 3H), 7.34–7.28 (m, 2H), 2.61 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 135.0, 130.8, 130.3, 129.5, 129.1, 125.7, 108.6, 108.0, 22.9. Anal. Calcd for C₁₁H₈N₂S₂: C, 56.87; H, 3.47; N, 12.06%. Found: C, 56.77; H, 3.40; N, 12.01%.

(*E*)-Ethyl 3-Phenyl-2,3-dithiocyanatoacrylate (**3s**). Colorless solid (206 mg, 71%), mp 104–106 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.51–7.48 (m, 3H), 7.21–7.18 (m, 2H), 4.42–4.37 (m, 2H), 1.39 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (CDCl₃, 100

MHz): δ 163.5, 159.1, 136.1, 131.4, 129.7, 127.4, 113.1, 108.8, 108.7, 64.4, 14.1. Anal. Calcd for $C_{13}H_{10}N_2O_2S_2$: C, 53.78; H, 3.47; N, 9.65%. Found: C, 53.72; H, 3.40; N, 9.57%.

(*E*)-2-(2-Thiocyanatovinyl)pyridine (**4a**). Colorless gummy mass (142 mg, 88%); 1H NMR ($CDCl_3$, 400 MHz): δ 8.61 (d, J = 4.8 Hz, 1H), 7.73–7.69 (m, 1H), 7.25–7.23 (m, 1H), 7.20–7.16 (m, 1H), 6.80 (d, J = 9.6 Hz, 1H), 6.69 (d, J = 9.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.9, 147.6, 137.0, 127.0, 123.8, 123.5, 122.2, 115.7. Anal. Calcd for $C_8H_6N_2S$: C, 59.24; H, 3.73; N, 17.27%. Found: C, 59.18; H, 3.82; N, 17.34%.

Dimethyl 2-Thiocyanatomaleate (**4b**). Yellow oil (179 mg, 89%); 1H NMR ($CDCl_3$, 400 MHz): δ 6.85 (s, 1H), 3.95 (s, 3H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.0, 161.9, 138.4, 126.2, 108.7, 54.3, 53.1. Anal. Calcd for $C_7H_7NO_4S$: C, 41.79; H, 3.51; N, 6.96%. Found: C, 41.70; H, 3.40; N, 6.87%.

(1,2-Dithiocyanatoethyl)benzene (**6a**).³⁹ White solid (149 mg, 72%); mp 102–104 °C; 1H NMR ($CDCl_3$, 400 MHz): δ 7.47–7.45 (m, 3H), 7.39–7.36 (m, 2H), 4.67–4.63 (m, 1H), 3.81–3.76 (m, 1H), 3.66–3.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.2, 130.5, 129.8, 127.7, 110.3, 109.9, 51.6, 38.3.

1-(1,2-Dithiocyanatoethyl)-4-methylbenzene (**6b**).³⁸ White solid, (187 mg, 80%), mp 99–101 °C; 1H NMR ($CDCl_3$, 400 MHz): δ 7.25 (s, 4H), 4.66–4.62 (m, 1H), 3.80–3.75 (m, 1H), 3.64–3.59 (m, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.7, 131.0, 130.4, 127.5, 110.4, 110.1, 51.5, 38.3, 21.4.

1-Chloro-4-(1,2-dithiocyanatoethyl)benzene (**6c**).³⁹ White solid, (191 mg, 75%), mp 88–90 °C; 1H NMR ($CDCl_3$, 400 MHz): δ 7.45–7.42 (m, 2H), 7.34–7.31 (m, 2H), 4.64–4.60 (m, 1H), 3.78–3.73 (m, 1H), 3.61–3.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.5, 132.8, 130.1, 129.0, 110.1, 109.6, 50.9, 38.0.

1-Bromo-4-(1,2-dithiocyanatoethyl)benzene (**6d**).³⁹ White solid, (209 mg, 70%), mp 90–92 °C; 1H NMR ($CDCl_3$, 400 MHz): δ 7.62–7.59 (m, 2H), 7.28–7.25 (m, 2H), 4.62–4.58 (m, 1H), 3.79–3.74 (m, 1H), 3.60–3.54 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 133.3, 133.1, 129.2, 124.8, 110.0, 109.4, 50.9, 38.0.

(1,2-Dithiocyanatoethane-1,1-diyl)dibenzene (**6e**). Pale yellow gummy mass (225 mg, 76%); 1H NMR ($CDCl_3$, 400 MHz): δ 7.45–7.37 (m, 6H), 7.34–7.32 (m, 4H), 4.02 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.1, 129.2, 129.1, 126.2, 111.3, 72.2, 46.7. Anal. Calcd for $C_{16}H_{12}N_2S_2$: C, 64.84; H, 4.08; N, 9.45%. Found: C, 64.72; H, 4.02; N, 9.35%.

General Procedure for the Synthesis of Compounds

8. A mixture of alkene (**5**, 1 mmol), KSeCN (288 mg, 2 mmol), and sodium persulfate (238 mg, 1 mmol) was taken in a dry sealed tube. 1,2-DCE (2 mL) was added to the mixture, and the resulting mixture was stirred at room temperature for 3 h. After completion of the reaction (TLC), the solvent (1,2-DCE) was evaporated in a rotary evaporator under reduced pressure, and the crude reaction mixture was purified by column chromatography on silica gel (60–120 mesh) using petroleum ether and ethyl acetate as eluents.

(1,2-Diselenocyanatoethyl)benzene (**8a**). White solid (235 mg, 75%), mp 105–107 °C; 1H NMR ($CDCl_3$, 400 MHz): δ 7.45–7.44 (m, 3H), 7.39–7.37 (m, 2H), 5.01–4.97 (m, 1H), 4.05–4.01 (m, 1H), 3.90–3.84 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.8, 130.4, 129.9, 127.7, 101.2, 100.0, 48.2, 33.9; ^{77}Se NMR (76 MHz, $CDCl_3$): δ 240.4, 240.2. Anal.

Calcd for $C_{10}H_8N_2Se_2$: C, 38.24; H, 2.57; N, 8.92%. Found: C, 38.14; H, 2.51; N, 8.83%.

1-Bromo-4-(1,2-diselenocyanatoethyl)benzene (**8b**). White solid (282 mg, 72%), mp 118–120 °C; 1H NMR ($CDCl_3$, 400 MHz): δ 7.53–7.49 (m, 2H), 7.22–7.18 (m, 2H), 4.87–4.83 (m, 1H), 3.97–3.93 (m, 1H), 3.75–3.69 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 133.1, 132.2, 129.2, 124.6, 100.7, 99.8, 47.4, 33.4; ^{77}Se NMR (76 MHz, $CDCl_3$): δ 245.1, 244.8; Anal. Calcd for $C_{10}H_7BrN_2Se_2$: C, 30.56; H, 1.80; N, 7.13%. Found: C, 30.48; H, 1.73; N, 7.10%.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01762.

Light-mediated reaction study: photocatalysis reaction of alkyne; structure determination (X-ray crystallographic data for **3s**); and NMR spectra of all the synthesized compounds (PDF).

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.M. acknowledges the financial support from the DST-RSF Major Research Project (ref. no. INT/RUS/RSF/P-08). S.S. and G.V.Z. acknowledge the financial support from the Russian Science Foundation—Russia (ref. # 18-73-00301). The authors are thankful to the DST-FIST and UGC-SAP programme of the Department of Chemistry, Visva-Bharati University.

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